David Topping
Editor of Atmospheric Chemistry and Physics
University of Manchester, Centre for Atmospheric Science

Dear David,

Listed below are our responses to the comments from reviewer 1 and 2. The reviewer's comments are in bold type and our responses are in normal text. We thank the referees for carefully reading our manuscript and for excellent comments.

Sincerely,
Allan Bertram
Professor of Chemistry
University of British Columbia

Referee #1

Major comments:

The paper is framed as a negative result, but the authors could increase its impact (or at least its interest level) by providing a better justification for the study in the introduction. This justification eventually comes in the last paragraph of the discussion: the presence of large molecular weight organics are thought to contribute to increases in particle viscosity, which could eventually make liquid-liquid phase separation kinetically difficult. Particles are more likely to become highly viscous at low temperatures, hence the need to see if large MW organics can affect liquid-liquid phase separation, especially at low temperatures.

To address the referee's comments, in the Introduction of the revised manuscript we have added a discussion on why there is reason to believe that the two parameters studied may influence LLPS. Specifically we have added the following text:

"Molecular weight of the organic molecules is of interest because viscosity of organic-inorganic salt mixtures can depend roughly on the molecular weight of the organic species, and at high molecular weights, liquid-liquid phase separation may become kinetically inhibited in highly viscous solutions. The effect of molecular weight of the organic material on the occurrence of liquid-liquid phase separation in mixed organic-inorganic salt particles has not been explored.

Temperature is of interest since temperature ranges from approximately 220 to 300 K in the troposphere, and temperature can influence the thermodynamics and kinetics of liquid-liquid phase separation. As an example of the effect of temperature on the thermodynamics of liquid-liquid phase transitions consider the binary mixture of water and butanol. At room temperature the binary mixture is partially immiscible. But as the temperature increases the region of immiscibility decreases until the upper critical solution temperature is reached. At higher temperatures the binary mixture is completely miscible. Certain mixtures can also have lower critical solution temperatures due to an increase in hydrogen bonding as the solution temperature decreases (Levine. 2009). Temperature may also influence the kinetics of liquid-liquid phase transitions. Some mixtures of organic species and inorganic salts can become highly viscous at lower temperatures and low relative humidities (Tong et al., 2011; Zobrist et al., 2008; Koop et al., 2011; Zobrist et al., 2011; Murray, 2008; Mikhailov et al., 2009; Saukko et al., 2012). At these low temperatures and relative humidities, liquid-liquid phase separation may be kinetically inhibited due to diffusion limitations. Only two studies have investigated liquid-liquid phase separation in mixed organic-inorganic salt particles at temperatures below 290 K."

Why do large MW and low temperatures have so little effect on liquid-liquid phase separation in the data collected?

A possible reason that a stronger dependence on temperature was not observed in the studies with organic-ammonium sulfate particles may be because for the systems studied the particles either didn't undergo liquid-liquid phase separation or the SRH was relatively high (> 65% RH). For the cases where liquid-liquid phase separation did not occur, an increase in viscosity from a decrease in temperature is not expected to change the results. For cases where the SRH was relatively high (> 65% RH), the water content in the particles was also likely high. Since water is a plasticizer, high water contents can lead to low viscosities and high diffusion rates. In this case, unless the temperature is very low, liquid-liquid phase separation is not expected to be kinetically inhibited. To address the referee's comment, we have added this discussion to the revised manuscript. See Section 3.2 in the revised manuscript.

Are the systems studied likely to become viscous at or above the temperatures and SRH levels used, or only below? Most critically, have the authors tested the effects of high viscosity on liquid-liquid phase separation using these chemical systems, or not?

To fully answer this question, one would need to know the viscosities as a function of relative humidity and temperature for the systems studied. To our knowledge, this information is not available for many of the systems we studied. To at least partially address the referee's comments, we have added to the revised manuscript the glass transition temperatures of the organic compounds studies when available. See Tables 1 and 2 in the revised manuscript.

Finally, what are the most likely reasons for the divergent behavior of organic compounds in the "maybe" zone of 0.57 < O/C < 0.83, where some compounds cause liquid-liquid phase separation, and others don't?

Song et al. 2012b showed that in the range of 0.56<O:C<0.8 the SRH can depend on the type of organic functional groups. Hence, a possible reason for the divergent behavior of organic compounds in the zone of 0.57 <O:C<0.83 is organic functional groups. To address the referee's comments, in the revised manuscript we have pointed out that measurements have also illustrated that the type of functional groups can influence the relative humidity required for liquid-liquid phase separation when the O:C of the organic material is in the range of approximately 0.5 to 0.8.

Other comments:
p. 23350 line 1: In the intro, the "frequently observed" liquid-liquid phase separation range is stated as O/C = 0.5 to 0.8 based on earlier studies. This data shows that the range is now 0.57 to 0.8 (and two pages earlier, 0.57 to 0.83). Here, the manuscript states that these ranges are consistent with each other, but they seem to be creeping upward. Are these differences significant, or is there some uncertainty in the O/C "borders" of liquid-liquid phase separation behavior that need to be acknowledged?

The ranges will depend slightly on which organic molecules are studied. Hence, there is some uncertainty in the O/C "borders". To address the referee's comments we have added this information to the revised manuscript. See Section 3.1.

p. 23350 line 10: While it may be true that SRH is "not a strong function of temperature," many of the organic compounds show trends that appear to be statistically significant in Figures 4 and 5. Further analysis to determine the level of significance of these trends would be appropriate.

To determine the level of significance of the temperature dependent trends, we carried out a linear regression analysis. In short, 5 out of the 12 systems studied had a high correlation coefficient (r≥0.94) and low p-value (≤0.06). In the revised manuscript, this information has been added to Section 3.2 and the linear regression analysis has been included in the Supplementary Material.

p. 23350 line 18: The O/C range of atmospheric particles also overlaps the range where liquid-liquid phase separation is frequently observed, and part of the range where it is never observed. So while the statement that "liquid-liquid phase separation is common in atmospheric particles" must be true, to be fair one could also state that particles that do not undergo liquid-liquid phase separation are also common.

This is a good point. In the revised manuscript we have also stated that particles that do not undergo liquid-liquid phase separation are also common. See Section 3.2 and Section 4.

Table 1: It would be helpful to add a column listing the functional groups present in these materials, like in Table 2.

As suggested, we have added a column of functional groups to Table 1.

Figure 3: I find the Sigmoidal-Boltzmann fit to be unsatisfying for the data with O/C ratios between 0.57 and 1. How can a continuous function fit what is essentially a discontinuous data set?

To address the referee's comments the Sigmoidal-Boltzmann fit has been removed from the revised manuscript.

Technical corrections

p. 23343 line 26 – p. 23344 line 7: Rhetorical question: Can there be too many references? Perhaps these nine lines of references could be split into two groups – references about efflorescence and deliquesce and those about liquid-liquid phase separation.

We have split the references into two groups, as suggested.

p. 23344 line 15: This is a strange statement. Mixing in an organic compound can modify the deliquescence and efflorescence relative humidities of an inorganic aerosol component, but liquid-liquid phase separation reverses that modification and makes the particle effloresce and deliquesce at nearly the same RH as pure inorganic aerosol particles. Perhaps a statement using the term "mitigate" instead of "modify" would be clearer.

We have revised this sentence to improve clarity. The revised sentence is listed below:

"Liquid-liquid phase separation can also influence the deliquescence and efflorescence relative humidity in mixed organic-inorganic salt particles (Bertram et al., 2011; Smith et al., 2012; Song et al., 2013)."

p. 23344 line 23: This paragraph repeatedly uses the phrase "studies have shown. . ."

We have revised this paragraph to reduce the redundancy. The revised paragraph is listed below:

"Recent work has investigated different parameters that influence liquid-liquid phase separation in particles containing mixtures of organic species and inorganic salts (You et al., 2014). Understanding the parameters that affect these transitions is necessary for predicting these phase transitions in atmospheric particles. Studies have shown that O:C is an important parameter for predicting liquid-liquid phase separation in these particles, with this phase transition always observed for O:C less than 0.5, frequently observed for O:C values between 0.5 and 0.8, and never observed for O:C values greater than 0.8 (Bertram et al., 2011; Song et al., 2012a, b; You et al., 2013). Measurements have also illustrated that the type of functional groups can also influence the relative humidity required for liquid-liquid phase separation when the O:C of the organic material is in the range of approximately 0.5 to 0.8 (Song et al., 2012b). On the other hand, the occurrence of liquid-liquid phase separation is not a strong function of the OIR or the number of organic species (Marcolli and Krieger, 2006; Ciobanu et al., 2009; Bertram et al., 2011; Song et al., 2012a, b; Schill and Tolbert, 2013). In addition, the occurrence of liquid-liquid phase separation may not be a strong function of the type of inorganic salt for O:C ≥ 0.8 and ≤ 0.5, but, in the range of 0.5 to 0.8, the occurrence of liquid-liquid phase separation can depend on the salt type (You et al. 2013)."

Referee #2
Major comments:

The authors present experimental data focusing on liquid-liquid phase separation (LLPS) in aqueous solution droplets for a set of organics mixed with ammonium sulfate. Specifically, they look at the effect of molecular mass of the organic compound and temperature on the onset relative humidity (SRH) of LLPS. The find negligible influences for both parameters for the systems they studied. The paper is well written and the conclusions are clearly supported by the experimental data. However, what is missing is a discussion why there is reason to believe that the two parameters studied (molecular mass and temperature) should influence LLPS at all.

To address the referee's comments in the Introduction of the revised manuscript we have added a discussion on why there is reason to believe that the two parameters studied may influence LLPS. For more details see response to Referee #1.

The last paragraph before the conclusion section seems to indicate that the authors think of kinetic limitations to LLPS. The argument being that higher molecular mass organics exhibit high viscosity at lower temperature and hence diffusion may kinetically inhibit LLPS on atmospherically relevant timescales. Of course, if this is the argument the authors have in mind, they should look for a system with high molecular mass but even more important low SRH, because viscosity (and diffusivity) depends strongly on water content in the droplet. From their previous studies (You et al., 2013) a system with low water content at the onset of LLPS is α,4-dihydroxy-3-methoxybenzeneacetic acid mixed with ammonium bisulfate (SRH = 38 %).

Studies of LLPS in α,4-dihydroxy-3methoxybeneacetic acid mixed with ammonium bisulfate is a great idea. To address the referee's comments we have gone back and studied this system. The results from this system are included in the revised manuscript and plotted in a new figure (Figure 6). Thank you for the great suggestion!

It is not quite clear to me why they choose the systems they studied (specifically, the type of salt and the specific OIR).

In the revised manuscript we have more clearly state why we choose the systems we studied. Listed below information included in the revised manuscript that explains why we choose the systems we studied.

"Particles consisting of ammonium sulfate mixed with one of twenty organic species were studied (see Table 2) at 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K, as well as 290 ± 1 K for a few of these particle types. For these studies, we chose the same particle types previously studied by You et al. (2013) at 290 ± 1 K. These particle types cover a wide range of O:C values and included functional groups found in atmospheric particles. Also, ammonium sulfate is one of the most common inorganic salts found in the atmosphere. In addition to picking the particles types previously studied by You et al. (2013), we also studied two additional organic species mixed with ammonium sulfate. These two organic species were raffinose and poly(ethylene glycol) diacrylate. These two species were chosen since they had relatively high molecular weights. An OIR value of 2.0 ± 0.1 was used in all the studies, consistent with You et al. (2013). The glass transition temperatures of the organic species studied cover the range of at least 192 K to 396 K."

And

"Particles containing ammonium sulfate mixed with one of ten organic species were studied at 290 ± 1 K (see Table 1). Most of previous laboratory studies of liquid-liquid phase separation in particles containing organic species mixed with ammonium sulfate used organic species with molecular weight less than 200 Da (Bertram et al., 2011; Song et al., 2012a, b; You et al., 2013). To complement these previous studies, in the current study we investigated particles containing ammonium sulfate and organic species with molecular weight ranging from 180 to 1153 Da (see Table 1). The specific organic species selected for these studies (Table 1) also had a relatively wide range of O:C values. The glass transition temperatures of the organics studied covered at least the range of 223 K to 412 K (see Table 1). In all the studies, the organic-to-inorganic mass ratio (OIR) was 2.0 ± 0.1. This value was chosen so that the current studies could be compared with the previous studies by You et al. (2013), who also used an OIR = 2.0 ± 0.1. In addition, this OIR value is in the range of OIR values observed in many field studies (Zhang et al., 2007; Jimenez et al., 2009)."

And

"In addition to studying particles consisting of ammonium sulfate mixed with one of twenty organic species, we also studied particles containing ammonium bisulfate mixed with α,4-dihydroxy-3-methoxybenzeneacetic acid at temperatures of 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K. This system was studied since it has a low SRH-value (38%) at 290 ± 1 K and hence has relatively low water content at the onset of liquid-liquid phase separation."

And how about thermodynamic reasons for an influence of molecular mass and/or temperature on LLPS? Why I do not see any immediate reason for molecular mass influencing miscibility of ternary mixtures of organic, water and salt, temperature could be a very significant parameter. It is well known that binary aqueous organics exhibiting a miscibility gap show an upper critical solution point which is the highest temperature at which two phases coexist because of the temperature dependence of the entropy of mixing. (This point may be not accessible experimentally because its temperature is higher than the boiling temperature of the mixture.) Some aqueous systems show in addition a lower critical solution temperature, because of the temperature dependence of the hydrogen bonding network of the organic compound in water. To be specific, for example polypropylene glycol (425) - one of the systems studied in the paper – show a lower critical solution temperature of about 50_C (Malcom and Rowlinson, 1957), i.e. it is miscible at room temperature at any ratio with water, while at higher temperatures two phases coexist in equilibrium. The results reported in the manuscript indicate that at an organic to inorganic ratio (OIR) of 2 (as chosen by the authors) the miscibility gap is extended very significantly to lower temperatures. Here the authors could have studied the system at higher OIR ratios and still observe LLPS if it occurred because the volume ratio of the two phases would be significant at intermediate RH even for low salt concentrations. Does a lower critical solution temperature still exist for small to moderate salt concentrations? Of course, this would mean a strong dependence on SRH with temperature as well. The authors may argue that high OIR is not atmospherically relevant, but extending (or at least discussing) the more basic physical chemistry aspects would make it more interesting and relevant at least in my view.

Thank you for the feedback. To address the referee's comments in the Introduction we have added thermodynamic reasons for an influence of temperature on LLPS. See discussion above. In addition we have added the following text to the Results and Discussion:

"Based on our results, particles containing poly(propylene glycol) and ammonium sulfate had SRH values ranging from 87.7 to 94.1% as the temperature ranged from 244 to 290 K. Solutions of water and poly(propylene glycol) show a lower critical solution temperature of approximately 50 ^{o}C. A comparison between this result and our current results indicate that the lower critical solution temperature is decreased significantly when ammonium sulfate is added to mixtures of poly(propylene glycol) and water."

Minor comments:

In the introduction you state that the occurrence of LLPS is not a strong function of the type of the inorganic salt. However, in You et al. (2013) you show that the type of salt becomes significant for an O:C ratio between 0.5 and 0.8 which may be quite significant in an atmospheric context.

Thank you for this comment. To address the referee's comment, the statement that the referee referred to has been modified to the following in the revised manuscript:

"In addition, the occurrence of liquid-liquid phase separation may not be a strong function of the type of inorganic salt for O:C ≥ 0.8 and ≤ 0.5. However, in the range of 0.5 to 0.8, the occurrence of liquid-liquid phase separation can depend on the salt type."

In section 2.1 you state that the RH sensor was calibrated using the deliquescence humidity of ammonium sulfate. It is not absolutely clear to me, but I assume the sensor is at room temperature? Does your calibration mean that you use one calibration point only? Could you please describe your calibration and your estimate of RH accuracy in more detail?

The hygrometer was calibrated prior to experiments at each temperature (244 ± 1 K, 263 ± 1 K, 278 ± 1 K, and 290 ± 1 K) by measuring the deliquescence relative humidity (DRH) of ammonium sulfate particles, and comparing the measured DRH value to the DRH valued predicted with Extended Aerosol Inorganic Model (E-AIM model) (Clegg et al. 1998). The uncertainty (2σ) of the hygrometer was ± 2.5 % RH after calibration, based on reproducibility of the DRH measurements. This information has been added to the revised manuscript in Section 2.1.

Of the twelve systems which show LLPS, most of those exhibiting a significant trend in temperature show a decrease in SRH with decreasing temperature. Could you please comment on this? It may be expected if there would be a closed loop miscibility gap of which you probe the lower temperature part?

As mentioned above, to determine the level of significance of the temperature dependent trends, we carried out a linear regression analysis. In short, 5 out of the 12 systems studied had a high correlation coefficient ($r \geq 0.94$) and low p-value (≤ 0.06). In the revised manuscript, this information has been added in Section 3.2, and the linear regression analysis has been added to the Supplementary Material. In addition, we have point out that a decrease in SRH with a decrease in temperature may be expected if there is a closed loop miscibility gap and the measurements are probing the lower temperature region of the closed loop.

Revised manuscript and supplementary material are below:

Effects of molecular weight and temperature on liquid-liquid phase separation in particles containing organic species and inorganic salts

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Abstract

Atmospheric particles containing organic species and inorganic salts may undergo liquid-liquid phase separation when the relative humidity varies between high and low values. To better understand the parameters that affect liquid-liquid phase separation in atmospheric particles, we studied the effects of molecular weight and temperature on liquid-liquid phase separation in particles containing one organic species mixed with either ammonium sulfate or ammonium bisulfate. In the molecular weight dependent studies, we measured liquid-liquid phase separation relative humidity (SRH) in particles containing ammonium sulfate and organic species with large molecular weights (up to 1153 Da). These results were combined with recent studies of liquid-liquid phase separation in the literature to assess if molecular weight is a useful parameter for predicting SRH. The combined results, which include results from 33 different particle types, illustrate that SRH does not depend strongly on molecular weight (i.e. a clear relationship between molecular weight and SRH was not observed). In the temperature dependent studies, we measured liquid-liquid phase separation in particles containing ammonium sulfate mixed with 20 different organic species at 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K, as well as 290 ± 1 K for a few of these particle types. These new results were combined with previous measurements of the same particle types at 290 ± 1 K. The combined SRH data illustrate that for the organic-ammonium sulfate particles studied the SRH does not depend strongly on temperature. At most the SRH varied by 9.7 % as the temperature varied from 290 to 244 K. The high SRH values (> 65%) in these experiments may explain the lack of temperature dependence. Since water is a plasticizer, high relative humidities can lead to high water contents, low viscosities and high diffusion rates in the particles. For these cases, unless the temperature is very low, liquid-liquid phase separation is not expected to be kinetically inhibited. The occurrence of liquid-liquid phase separation and SRH did depend strongly on temperature over the range of 290-244 K for particles containing α,4-dihydroxy-3-methoxybenzeneacetic acid mixed with ammonium bisulfate. For this particle type, a combination of low temperatures and low water content likely favored kinetic inhabitation of the liquid-liquid phase separation by slow diffusion rates in highly viscous particles. The combined results suggest that liquid-liquid phase separation is likely a common occurrence in atmospheric particles at temperatures from 244-290 K, although particles that do not undergo liquid-liquid phase separation are also likely common.

1 Introduction

A large fraction of particles in the atmosphere contains both organic species and inorganic salts (Murphy and Thomson, 1997; Murphy et al., 1998; Middlebrook et al., 1998; Buzorius et al., 2002; Murphy, 2005; Murphy et al., 2006; Tolocka et al., 2005; Chen et al., 2009; Pratt and Prather, 2010). Ammonium sulfate and ammonium bisulfate are both common inorganic salts in these particles (Dibb et al., 1996; Huebert et al., 1998; Talbot et al., 1998; Dibb et al., 2000; Lee et al., 2003). The types of organic species in these particles are numerous with only around 10% by mass of these organic species identified at the molecular level (Hamilton et al., 2004; Goldstein and Galbally, 2007; Decesari et al., 2006; Hallquist et al., 2009). Organic functional groups found in mixed organic-inorganic salt particles include carboxylic acids, alcohols, oxidized aromatic compounds, ethers, and esters (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006; Decesari et al., 2006; Hallquist et al., 2009; Takahama et al., 2011; Rogge et al., 1993; Saxena and Hildemann, 1996; Finlayson-Pitts and Pitts, 1997; Day et al., 2009; Gilardoni et al., 2009; Liu et al., 2009; Russell et al., 2009; Russell et al., 2011; Fu et al., 2011; Fuzzi et al., 2001). The molecular weight of organic molecules in these mixed particles is thought to range from less than 100 Da to as high as 1000 Da (Gao et al., 2004; Tolocka et al., 2004; Kalberer et al., 2004; Nguyen et al., 2010). In addition, the average oxygen-to-carbon elemental ratios (O:C) of the organic material in ambient particles generally range from 0.1 to 1.0 (Chen et al., 2009; Aiken et al., 2008; DeCarlo et al., 2008; Jimenez et al., 2009; Hawkins et al., 2010; Heald et al., 2010; Ng et al., 2010; Takahama et al., 2011), while the average organic-to-inorganic mass ratios (OIR) of atmospheric particles generally range from 0.2 to 3.5 (Chen et al., 2009; Zhang et al., 2007; Jimenez et al., 2009).

When the relative humidity varies in the atmosphere, mixed organic-inorganic salt particles can undergo different phase transitions, including efflorescence and deliquescence (Martin, 2000; Brooks et al., 2002; Choi and Chan, 2002; Brooks et al., 2003; Chan and Chan, 2003; Wise et al., 2003; Braban and Abbatt, 2004; Pant et al., 2004; Parsons et al., 2004a; Badger et al., 2006; Chang and Pankow, 2006; Erdakos et al., 2006; Parsons et al., 2006; Salcedo, 2006; Ling and Chan, 2008; Treuel et al., 2009; Bodsworth et al., 2010). More recent laboratory measurements and calculations have focused on liquid-liquid phase separation (Clegg et al., 2001; Pankow, 2003; Marcolli and Krieger, 2006; Anttila et al., 2007; Buajarern et al., 2007; Zuend et al., 2008; Ciobanu et al., 2009; Kwamena et al., 2010; Prisle et al., 2010; Zuend et al., 2010; Bertram et al., 2011; Reid et al., 2011; Smith et al., 2011; Zuend et al., 2011; Krieger et al., 2012; Pöhlker et al., 2012; Smith et al., 2012; Song et al., 2012a, b; You et al., 2012; Zuend and Seinfeld, 2012; Drozd et al., 2013; Shiraiwa et al., 2013; Song et al., 2013; Veghte et al., 2013; You et al., 2013; Zuend and Seinfeld, 2013; Veghte et al., 2014). Liquid-liquid phase separation in the atmospheric particles can influence the partitioning of organic molecules between the gas and the particle phase (Seinfeld et al., 2001; Chang and Pankow, 2006; Zuend et al., 2010; Shiraiwa et al., 2013) and influence the reactive uptake of important gas-phase molecules, such as N_2O_5, into atmospheric particles (Anttila et al., 2006; Folkers et al., 2003; Escoreia et al., 2010; Cosman and

Bertram, 2008; Park et al., 2007; Thornton and Abbatt, 2005; McNeill et al., 2006; Gaston et al., 2014). Liquid-liquid phase separation can also influence the deliquescence and efflorescence relative humidity in mixed organic-inorganic salt particles (Bertram et al., 2011; Smith et al., 2012; Song et al., 2013). In addition, liquid-liquid phase separation can alter the ice nucleation properties of particles (Schill and Tolbert, 2013).

Recent work has investigated different parameters that influence liquid-liquid phase separation in particles containing mixtures of organic species and inorganic salts (You et al., 2014). Understanding the parameters that affect these transitions is necessary for predicting these phase transitions in atmospheric particles. Studies have shown that O:C is an important parameter for predicting liquid-liquid phase separation in these particles, with this phase transition always observed for O:C less than 0.5, frequently observed for O:C values between 0.5 and 0.8, and never observed for O:C values greater than 0.8 (Bertram et al., 2011; Song et al., 2012a, b; You et al., 2013). Measurements have also illustrated that the type of functional groups can also influence the relative humidity required for liquid-liquid phase separation when the O:C of the organic material is in the range of approximately 0.5 to 0.8 (Song et al., 2012b). On the other hand, the occurrence of liquid-liquid phase separation is not a strong function of the OIR or the number of organic species (Marcolli and Krieger, 2006; Ciobanu et al., 2009; Bertram et al., 2011; Song et al., 2012a, b; Schill and Tolbert, 2013). In addition, the occurrence of liquid-liquid phase separation may not be a strong function of the type of inorganic salt for O:C ≥ 0.8 and ≤ 0.5, but, in the range of 0.5 to 0.8, the occurrence of liquid-liquid phase separation can depend on the salt type (You et al. 2013).

In the following paper, we investigate if molecular weight of the organic material and temperature of the particles influence liquid-liquid phase separation in particles containing organic species and inorganic salts. Molecular weight of the organic molecules is of interest because viscosity of organic-inorganic salt mixtures can depend roughly on the molecular weight of the organic species, and at high molecular weights, liquid-liquid phase separation may become kinetically inhibited in highly viscous solutions. The effect of molecular weight of the organic material on the occurrence of liquid-liquid phase separation in mixed organic-inorganic salt particles has not been explored.

Temperature is of interest since temperature ranges from approximately 220 to 300 K in the troposphere, and temperature can influence the thermodynamics and kinetics of liquid-liquid phase separation. As an example of the effect of temperature on the thermodynamics of liquid-liquid phase transitions consider the binary mixture of water and butanol. At room temperature the binary mixture is partially immiscible. But as the temperature increases the region of immiscibility decreases until the upper critical solution temperature is reached. At higher temperatures the binary mixture is completely miscible. Certain mixtures can also have lower critical solution temperatures due to an increase in hydrogen bonding as the solution temperature decreases (Levine. 2009). Temperature may also influence the kinetics of liquid-liquid phase transitions. Some mixtures of organic species and inorganic salts can become highly viscous at lower temperatures and low relative humidities (Tong et al., 2011; Zobrist et al., 2008; Koop et al., 2011; Zobrist et al., 2011; Murray, 2008; Mikhailov et al., 2009; Saukko et al., 2012). At these low temperatures and relative humidities, liquid-liquid phase separation may be kinetically inhibited due to diffusion limitations. Only two studies have investigated liquid-liquid phase separation in mixed organic-inorganic salt particles at temperatures below 290 K. Bertram et al. reported that SRH results were similar at 273 K and 290 K for particles containing ammonium sulfate and 1,2,6-hexanetriol (Bertram et al., 2011). Schill and Tolbert reported that SRH results were similar for temperatures from 240 to 265 K for particles containing ammonium sulfate mixed with 1,2,6-hexanetriol and particles containing ammonium sulfate, 1,2,6-hexanetriol, and 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol (Schill and Tolbert, 2013).

Here we carried out a systematic study of the effect of molecular weight of the organic material on liquid-liquid phase separation at 290 ± 1 K. We first studied liquid-liquid phase separation in particles containing ammonium sulfate mixed with one of ten organic species, with molecular weights up to 1153 Da. The data from these studies were then combined with recent studies of liquid-liquid phase separation in particles reported in the literature (You et al., 2013) to assess if molecular weight is a useful parameter to predict the occurrence of liquid-liquid phase separation and the liquid-liquid phase separation relative humidity (SRH).

To gain a better understanding of the effect of temperature on liquid-liquid phase separation in mixed organic-inorganic salt particles, we investigated liquid-liquid phase separation in particles containing ammonium sulfate mixed with one of twenty organic species at 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K, respectively. Some of these particle types were also studied at 290 ± 1 K. These new data were combined with previous measurements of liquid-liquid phase separation at 290 ± 1 K by You et al. (You et al., 2013) to assess the effect of temperature on liquid-liquid phase separation in mixed organic-ammonium sulfate particles.

We also investigated liquid-liquid phase separation in particles containing ammonium bisulfate mixed with α,4-dihydroxy-3-methoxybenzeneacetic acid at temperatures of 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K. This system was studied since it has a relatively low SRH-value (38%) at 290 ± 1 K and, hence, has relatively low water content at the onset of liquid-liquid phase separation. In addition to temperature and molecular weight, water content is likely important for the kinetics of liquid-liquid phase separations, as the viscosity and diffusion rates within the particles are expected to be sensitive to water content (Koop et al. 2011; Renbaum-Wolff et al. 2013; Power et al. 2013; Kidd et al. 2014).

2 Experimental

2.1 Sample preparation and apparatus.

Solutions of ammonium sulfate or ammonium bisulfate and one organic species were prepared in high purity water (Millipore, 18.2 MΩ cm) with OIR of 2.0 ± 0.1. The solutions were then nebulized to produce submicron particles, which impacted onto a hydrophobic glass slide (Hampton Research) and coagulated into super-micron droplets. Water was then evaporated to generate mixed organic-inorganic salt particles with lateral dimensions ranging from 10 to 35 µm.

The glass slide supporting the mixed organic-inorganic salt particles was mounted to a temperature and relative humidity controlled flow cell, which was coupled to an optical reflectance microscope (Zeiss Axiotech; 50× objective) (Koop et al., 2000; Parsons et al., 2004b; Pant et al., 2006; Bodsworth et al., 2010). To control the relative humidity in the flow cell, dry and humidified nitrogen gas flows were combined and continuously passed through the cell. The total flow rate was approximately 1.5 L min^{-1}. While the RH was decreased, liquid-liquid phase separation was identified by monitoring the change in morphology of the particles. The relative humidity of the gas was determined with a chilled mirror hygrometer (General Eastern, Model 1311DR). The hygrometer was calibrated prior to experiments at each temperature (244 ± 1 K, 263 ± 1 K, 278 ± 1 K, and 290 ± 1 K) by measuring the deliquescence relative humidity (DRH) of ammonium sulfate particles, and comparing the measured DRH value to the DRH valued predicted with the Extended Aerosol Inorganic Model (E-AIM model) (Clegg et al. 1998). The uncertainty (2σ) of the hygrometer was ± 2.5 % RH after calibration based on reproducibility of the DRH measurements.

2.2 Molecular weight dependent studies.

Particles containing ammonium sulfate mixed with one of ten organic species were studied at 290 ± 1 K (see Table 1). Most of previous laboratory studies of liquid-liquid phase separation in particles containing organic species mixed with ammonium sulfate used organic species with molecular weight less than 200 Da (Bertram et al., 2011; Song et al., 2012a, b; You et al., 2013). To complement these previous studies, in the current study we investigated particles containing ammonium sulfate and organic species with molecular weight ranging from 180 to 1153 Da (see Table 1). The specific organic species selected for these studies (Table 1) also had a relatively wide range of O:C values. The glass transition temperatures of the organics studied covered at least the range of 223 K to 412 K (see Table 1). In all the studies, the organic-to-inorganic mass ratio (OIR) was 2.0 ± 0.1. This value was chosen so that the current studies could be compared with the previous studies by You et al. (2013), who also used an OIR = 2.0 ± 0.1. In addition, this OIR value is in the range of OIR values observed in many field studies (Zhang et al., 2007; Jimenez et al., 2009).

In a typical experiment, the RH in the cell was ramped down at a rate of 0.4-0.6% RH min^{-1}, while the temperature of the cell was held at 290 ± 1 K. At the same time, images of the particles were captured continuously until one of the following conditions occurred: liquid-liquid phase separation was observed, the particles effloresced, or the RH reached ≤ 0.5%. For each type of particle, experiments were repeated at least three times. All of the organic species were purchased from Sigma-Aldrich and had purities ≥ 95%, except for maltoheptaose, which had a purity ≥ 90%.

2.3 Temperature dependent studies.

Particles consisting of ammonium sulfate mixed with one of twenty organic species were studied (see Table 2) at 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K, as well as 290 ± 1 K for a few of these particle types. For these studies, we chose the same particle types previously studied by You et al. (2013) at 290 ± 1 K. These particle types cover a wide range of O:C values and included functional groups found in atmospheric particles. Also, ammonium sulfate is one of the most common inorganic salts found in the atmosphere. In addition to picking the particles types previously studied by You et al. (2013), we also studied two additional organic species mixed with ammonium sulfate. These two organic species were raffinose and poly(ethylene glycol) diacrylate. These two species were chosen since they had relatively high molecular weights. An OIR value of 2.0 ± 0.1 was used in all the studies, consistent with You et al. (2013). The glass transition temperatures of the organic species studied cover the range of at least 192 K to 396 K. In addition to studying particles consisting of ammonium sulfate mixed with one of twenty organic species, we also studied particles containing ammonium bisulfate mixed with α,4-dihydroxy-3-methoxybenzeneacetic acid at temperatures of 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K. As mentioned in the introduction, this system was studied since it has a low SRH-value (38%) at 290 ± 1 K and hence has relatively low water content at the onset of liquid-liquid phase separation.

The organic species studied were purchased from Sigma-Aldrich with purities ≥ 98%. All organics were used without further purification. In a typical temperature dependent experiment, the RH was ramped down at a rate of around 0.1- 0.5 % RH min^{-1}. Images were recorded in the same way as the molecular weight dependent studies.

3 Results and Discussion

3.1 Effect of molecular weight on liquid-liquid phase separation

Particles containing ammonium sulfate mixed with one of ten organic species were studied at 290 ± 1 K. In these studies organic species with large molecular weights (180 to 1153 Da) were used. The organic-to-inorganic mass ratio (OIR) was 2.0 ± 0.1 in all the studies. The results from these studies are listed in Table 3 as well as the data from You et al., who also studied particles with an OIR of 2.0 ± 0.1 at 290 ± 1 K (You et al., 2013). The combined data set in Table 3, which includes results of liquid-liquid phase separation for 33 different particle types, was used to determine the importance of molecular weight of the organic species on liquid-liquid phase separation.

In Figure 1, the data from Table 3 were plotted as a function of O:C and molecular weight. Open circles indicate liquid-liquid phase separation was observed and stars indicate liquid-liquid phase separation was not observed. No clear relationship between molecular weight and the occurrence of liquid-liquid phase separation was observed, however a relationship between occurrence of liquid-liquid phase separation and O:C was clear: liquid-liquid phase separation was always observed when O:C < 0.57 (orange hatched region), was never observed when O:C > 0.83 (green hatched region), and was frequently observed when O:C ranged from 0.57 to 0.83. This range is slightly different than the range previously measured (0.5 to 0.8) (Bertram et al. 2011; Song et al. 2012a, b; You et al. 2013), which is not surprising since this range is expected to change slightly with the type of organic molecules studied. As such, there is a small uncertainty in this range. In Figure 2, the SRH data from Table 3 were plotted as a function of molecular weight of the organic species. The colors of the symbols indicate the O:C of organic species in the mixed particles. Data at SRH = 0 % indicate liquid-liquid phase separation was not observed even at the lowest relative humidity studied. Similar to Figure 1, no correlation with molecular weight was apparent. For contrast, in Figure 3, we show the same SRH data plotted as a function of O:C of organic species with the color of the symbols representing the molecular weight of organic species. Consistent with previous results (Bertram et al., 2011; Song et al., 2012b), a correlation between SRH and O:C is apparent. These results suggest that O:C is more important for predicting the occurrence of liquid-liquid phase separation in atmospherically relevant mixed organic-ammonium sulfate particles compared with molecular weight.

3.2 Effect of temperature on liquid-liquid phase separation

In the temperature dependent experiments, particles containing ammonium sulfate mixed with one of twenty organic species were studied at 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K. Some of the particle types were also studied at 290 ± 1 K. The temperature dependent results are included in Table 4 as well as results from You et al., who studied most of the same types of particles but only at 290 ± 1 K (You et al., 2013). The combined SRH data from Table 4, which cover the temperature range of 290-244 K, were plotted in Figure 4A as a function of O:C of the organic species. The temperature dependent results show that for all the particle types studied and at all the temperatures studied liquid-liquid phase separation was always observed when O:C < 0.57, frequently observed when $0.57 \leq$ O:C < 0.8, and never observed when O:C ≥ 0.8. We conclude that the O:C range at which liquid-liquid phase separation was observed at 290-293 K in previous studies (Ciobanu et al., 2009; Bertram et al., 2011; Song et al., 2012b; You et al., 2013), is reasonably consistent with the range observed at temperatures down to 244 ± 1 K.

Figure 5 shows the same data as in Figure 4A, but displayed in a slightly different way. The SRH results for the twelve types of mixed organic-ammonium sulfate particles that underwent liquid-

liquid phase separation in Figure 4A, are shown as a function of temperature, with the colors of the symbols representing the O:C values of the organic species in the particles. For all the particle types included in Figure 5, the SRH varied by less than 9.7 % RH as the temperature varied from 244 to 290 K. Figure 4A and 5 illustrate that SRH is not a strong function of temperature for the particle types investigated. These results are consistent with earlier studies by Bertram et al. and Schill and Tolbert discussed in the Introduction. In the Supplementary Material we carried out a linear regression analysis to determine the level of significance of the temperature dependent trends observed in Figure 5. In short, five out of the twelve systems studied had a high correlation coefficient ($r \geq 0.94$) between temperature and SRH and an associated low p-value (≤ 0.06). A decrease in SRH with a decrease in temperature may be expected if there is a closed loop miscibility gap and the measurements are probing the lower temperature region of the closed loop.

Based on our results, particles containing poly(propylene glycol) and ammonium sulfate had SRH values ranging from 87.7 to 94.1 % as the temperature ranged from 244 to 290 K. Solutions of water and poly(propylene glycol) show a lower critical solution temperature of approximately 50 ^{o}C (Malcom and Rowlinson, 1957). A comparison between this result and our current results indicate that the lower critical solution temperature is decreased significantly when ammonium sulfate is added to mixtures of poly(propylene glycol) and water.

As mentioned in the introduction, some mixtures of organic species and inorganic salts can become highly viscous at lower temperatures and low relative humidities, and at these low temperatures and relative humidities, liquid-liquid phase separation may be kinetically inhibited due to diffusion limitations. A possible reason that a stronger dependence on temperature was not observed in the studies discussed above may be because for the systems studied the particles either didn’t undergo liquid-liquid phase separation or the SRH was relatively high (> 65% RH). For the cases where liquid-liquid phase separation did not occur, an increase in viscosity from a decrease in temperature is not expected to change the results. For cases where the SRH was relatively high (> 65% RH), the water content in the particles was also likely relatively high. Since water is a plasticizer, high water contents can lead to low viscosities and high diffusion rates. In this case, unless the temperature is very low, liquid-liquid phase separation is not expected to be kinetically inhibited.

Although SRH does not appear to be a strong function of the temperature for the organic-ammonium sulfate particle types studied over the temperature range of 244 to 290 K, SRH may be a strong function of temperature for these particles at temperatures lower than 244 K due to kinetic limitations or thermodynamic reasons. Additional studies of SRH at temperatures lower than 244 K are still needed for these particle types.

In Figure 6, SRH as a function of temperature is plotted for particles containing α,4-dihydroxy-3-methoxybenzeneacetic acid mixed with ammonium bisulfate. At 263 ± 1 K and warmer no strong dependence on temperature is observed, with an average SRH value of approximately 37.6 %. At 244 K, however, liquid-liquid phase separation was not observed. A likely explanation for this drastic decrease in the SRH is likely kinetic inhabitation of the liquid-liquid phase separation. Related, previous research has shown that efflorescence is inhibited in particles containing organic species and inorganic salts at low temperatures and low relative humidities likely due to diffusion limitations (Bodsworth et al., 2010). The studies with particles containing ammonium bisulfate and α,4-dihydroxy-3-methoxybenzeneacetic acid suggests that a combination of low temperatures (e.g. 244 K) and low relative humidities (e.g. approximately 38% RH) can lead to kinetic inhibition of liquid-liquid phase separation.

The average O:C of organic material in atmospheric particles has been measured at many locations in the Northern Hemisphere and in the Amazon and has been shown to range from 0.1 to 1.0 (Chen et al., 2009; Aiken et al., 2008; DeCarlo et al., 2008; Jimenez et al., 2009; Hawkins et al., 2010; Heald et al., 2010; Ng et al., 2010; Takahama et al., 2011). This range of O:C values is indicated in Figure 4B. The range of average O:C values measured in the atmosphere overlaps with the range of O:C values where liquid-liquid phase separation was observed at temperatures ranging from 244 to 290 K (Figure 4 B). This overlap suggests that liquid-liquid phase separation is likely a common occurrence in the atmosphere over this temperature range. Particles that do not undergo liquid-liquid phase separation are also expected to be common based on a comparison between our data and the range of O:C values found in the atmosphere.

4 Conclusions

The occurrence of liquid-liquid phase separation and SRH did not depend strongly on the molecular weight of the organic species at 290 ± 1 K, at least for the particle types studied. The occurrence of liquid-liquid phase separation and SRH also did not depend strongly on temperature over the range of 290- 244 K for particles containing ammonium sulfate mixed with one organic species. The SRH varied by at most 9.7 % RH as the temperature varied from 290 ± 1 K to 244 ± 1 K for the particle types studied. The high SRH values (> 65%) in these experiments may explain the lack of temperature dependence. Since water is a plasticizer, high relative humidities can lead to high water contents, low viscosities and high diffusion rates. For these cases, unless the temperature is very low, liquid-liquid phase separation is not expected to be kinetically inhibited. The occurrence of liquid-liquid phase separation and SRH did depend strongly on temperature over the range of 290-244 K for particles containing α,4-dihydroxy-3-methoxybenzeneacetic acid mixed with ammonium bisulfate. For this particle type, a combination of low temperatures and low water content likely favored kinetic inhabitation of the liquid-liquid phase separation by slow diffusion rates in highly viscous particles.

The combined results suggest that liquid-liquid phase separation is likely a common occurrence in the atmospheric particles at 290-244 K, although particles that do not undergo liquid-liquid phase separation are also likely common.

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Tables

Table 1. List of the ten organic species used in molecular weight dependent measurements. Each organic species was separately mixed with ammonium sulfate to make particles, and liquid-liquid phase separation was studied in these particles at 290 ± 1 K.

Compounds	Formula	Molecular weight (Da)	O:C	Functional group(s)	Glass transition temperature, T_g (K)	References for T_g
Glucose	$C_6H_{12}O_6$	180.2	1	alcohol, ether	296.1±3.1	Zobrist et al. 2008
Poly(ethylene glycol) bis(carboxymethyl) ether	$C_{2n+4}H_{4n+6}O_{n+5}$	250	0.83	alcohol, ether	-	-
Sucrose	$C_{12}H_{22}O_{11}$	342.3	0.92	alcohol, ether	335.7±3.6	Zobrist et al. 2008
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	400	0.56	alcohol, ether	223	Faucher et al. 1966
Ouabain	$C_{29}H_{44}O_{12}$	584	0.41	alcohol, ether, ester, C-C double bonds	373[a]	Koop et al. 2011
Raffinose	$C_{18}H_{32}O_{16}$	594.5	0.89	alcohol, ether	395.7±21.6	Zobrist et al. 2008
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	600	0.54	alcohol, ether	231	Faucher et al. 1966
Maltopentaose	$C_{30}H_{52}O_{26}$	829	0.87	alcohol, ether	398	Slade and Levine 1994
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	900	0.53	alcohol, ether	231-245	Faucher et al. 1966
Maltoheptaose	$C_{42}H_{72}O_{36}$	1153	0.86	alcohol, ether	412	Slade and Levine 1994

[a] T_g values are estimates based on the melting points of those organic compounds using the results from Koop et al. 2011.

\- Literature data not available

Table 2. Summary of the twenty organic species used in temperature dependent experiments. Each organic species was separately mixed with ammonium sulfate to make particles, and liquid-liquid phase separation was studied in these particles at 244 ± 1 K, 263 ± 1 K and 278 ± 1 K. Two of the organic species (poly(ethylene glycol) diacrylate and raffinose) mixed with ammonium sulfate were also studied at 290 ± 1 K.

Compounds	Formula	O:C	Molecular weight (Da)	Functional group(s)	Glass transition temperature T_g (K)	References for T_g
2,5-hexanediol	$C_6H_{14}O_2$	0.33	118.2	alcohol	192.4 ± 1.3	Zobrist et al. 2008
Poly(propylene glycol)	$C_{3n}H_{6n+2}O_{n+1}$	0.38	425	alcohol, ether	-	-
Poly(ethylene glycol) diacrylate	$C_{2n+6}H_{4n+6}O_{n+3}$	0.5	575	ester, ether, C-C double bond	-	-
Poly(ethylene glycol) 900	$C_{2n}H_{4n+2}O_{n+1}$	0.53	900	alcohol, ether	231-245[a]	Faucher et al. 1966
α,4-dihydroxy-3-methoxybenzeneacetic acid	$C_9H_{10}O_5$	0.56	198.2	alcohol, aromatic, carboxylic acid, ether	293.6 ± 6.6	Zobrist et al. 2008
Diethylmalonic acid	$C_7H_{12}O_4$	0.57	160.2	carboxylic acid	282[b]	Koop et al. 2011
3,3-dimethylglutaric acid	$C_7H_{12}O_4$	0.57	160.2	carboxylic acid	261[b]	Koop et al. 2011
2,5-hydroxybenzoic acid	$C_7H_6O_4$	0.57	154.2	carboxylic acid, aromatic	225[b]	Koop et al. 2011
Poly(ethylene glycol) 300	$C_{2n}H_{4n+2}O_{n+1}$	0.58	300	alcohol, ether	203-223	Faucher et al. 1966
Poly(ethylene glycol) 200	$C_{2n}H_{4n+2}O_{n+1}$	0.63	200	alcohol, ether	203	Faucher et al. 1966
Poly(ethylene glycol) bis(carboxymethyl) ether	$C_{2n+4}H_{4n+6}O_{n+5}$	0.63	600	alcohol, ether	-	-
2-methylglutaric acid	$C_6H_{10}O_4$	0.67	146.1	carboxylic acid	247[b]	Koop et al. 2011
2,2-dimethylsuccinic acid	$C_6H_{10}O_4$	0.67	146.2	carboxylic acid	289[b]	Koop et al. 2011
Diethyl-L-tartrate	$C_8H_{14}O_6$	0.75	206.2	alcohol, ether	-	-
Glycerol	$C_3H_8O_3$	1.00	92.1	alcohol	193.3 ± 1.1	Zobrist et al. 2008
Glutaric acid	$C_5H_8O_4$	0.8	132.1	carboxylic acid	258[b]	Koop et al. 2011

Levoglucosan	$C_6H_{10}O_5$	0.83	162.1	alcohol, ester	319[b]	Koop et al. 2011
Raffinose	$C_{18}H_{32}O_{16}$	0.89	594.5	alcohol, ester	395.7 ± 21.6	Zobrist et al. 2008
Citric acid	$C_6H_8O_7$	1.17	192.1	alcohol, carboxylic acid	280.1	Bodsworth et al. 2010
Malonic acid	$C_3H_4O_4$	1.33	104.1	carboxylic acid	286[b]	Koop et al. 2011

[a] T_g value is an estimate based on the molecular weight of the ploy (ethylene glycol 900) from Faucher et al. 1966.

[b] T_g values are estimates based on the melting points of those organic compounds using the results from Koop et al. 2011.

- Literature data not available

Table 3. Combined data set used to assess the effect of molecular weight on SRH in mixed organic-ammonium sulfate particles. This data set includes the ten types of particles studied here (see Table 1) and the SRH results of twenty-three types of particles containing single organic species and ammonium sulfate studied by You et al. (2013). OIR = 2.0 ± 0.1 in all the experiments. Uncertainties are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration.

Compounds	Formula	Molecular weight (Da)	O:C	SRH (%)	Reference
Glycerol	$C_3H_8O_3$	92.1	1	Not observed	You et al. (2013)
Malonic acid	$C_3H_4O_4$	104.1	1.33	Not observed	You et al. (2013)
Maleic acid	$C_4H_4O_4$	116.1	1	Not observed	You et al. (2013)
2,5-hexanediol	$C_6H_{14}O_2$	118.2	0.33	88.8 ± 7.1	You et al. (2013)
Glutaric acid	$C_5H_8O_4$	132.1	0.8	Not observed	You et al. (2013)
Malic acid	$C_4H_6O_5$	134.1	1.25	Not observed	You et al. (2013)
1,2,6-hexanetriol	$C_6H_{14}O_3$	134.2	0.5	76.7 ± 6.2	You et al. (2013)
2-methylglutaric acid	$C_6H_{10}O_4$	146.1	0.67	75.3 ± 6.4	You et al. (2013)
2,2-dimethylsuccinic acid	$C_6H_{10}O_4$	146.2	0.67	Not observed	You et al. (2013)
2,5-hydroxybenzoic acid	$C_7H_6O_4$	154.2	0.57	Not observed	You et al. (2013)
Diethylmalonic acid	$C_7H_{12}O_4$	160.2	0.57	89.2 ± 4.2	You et al. (2013)
3,3-dimethylglutaric acid	$C_7H_{12}O_4$	160.2	0.57	89.1 ± 6.9	You et al. (2013)
Levoglucosan	$C_6H_{10}O_5$	162.1	0.83	Not observed	You et al. (2013)
Glucose	$C_6H_{12}O_6$	180.2	1	Not observed	Current study
Suberic acid monomethyl ester	$C_9H_{16}O_4$	188.2	0.44	100 ± 6.2	You et al. (2013)
Citric acid	$C_6H_8O_7$	192.1	1.17	Not observed	You et al. (2013)
α,4-dihydroxy-3-methoxybenzeneacetic acid	$C_9H_{10}O_5$	198.2	0.56	72.6 ± 6.3	You et al. (2013)
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	200	0.63	79.8 ± 7.4	You et al. (2013)
Diethyl-L-tartrate	$C_8H_{14}O_6$	206.2	0.75	90.2 ± 6.6	You et al. (2013)
Poly(ethylene glycol) bis(carboxymethyl) ether	$C_{2n+4}H_{4n+6}O_{n+5}$	250	0.83	67.6 ± 6.2	Current study
Diethyl sabacate	$C_{14}H_{26}O_4$	258.4	0.29	100 ± 6.2	You et al. (2013)
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	300	0.58	86.7 ± 6.4	You et al. (2013)
Sucrose	$C_{12}H_{22}O_{11}$	342.3	0.92	Not observed	Current study

Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	400	0.56	88.3 ± 6.6	Current study
Poly(propylene glycol)	$C_{3n}H_{6n+2}O_{n+1}$	425	0.38	94.1 ± 6.7	You et al. (2013)
Poly(ethylene glycol) diacrylate	$C_{2n+6}H_{4n+6}O_{n+3}$	575	0.5	94.7 ± 6.2	You et al. (2013)
Ouabain	$C_{29}H_{44}O_{12}$	584	0.41	90.1 ± 6.8	Current study
Raffinose	$C_{18}H_{32}O_{16}$	594.5	0.89	Not observed	Current study
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	600	0.54	89.5 ± 6.3	Current study
Poly(ethylene glycol) bis(carboxymethyl) ether	$C_{2n+4}H_{4n+6}O_{n+5}$	600	0.63	92.0 ± 6.3	You et al. (2013)
Maltopentaose	$C_{30}H_{52}O_{26}$	829	0.87	Not observed	Current study
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	900	0.53	92.9 ± 6.4	Current study
Maltoheptaose	$C_{42}H_{72}O_{36}$	1153	0.86	Not observed	Current study

Table 4. Combined data set used to determine the effect of temperature on SRH. This includes the measurements at 244 ± 1 K, 263 ± 1 K and 278 ± 1 K in the current studies (Table 2) and results from You et al. (2013) at 290 ± 1 K. OIR = 2.0 ± 0.1 in all the experiments. Uncertainties are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration.

Compound	O:C	SRH (%) at different temperatures			
		244 ± 1 K	263 ± 1 K	278 ± 1 K	290 ± 1 K
2,5-hexanediol	0.33	84.0 ± 8.3	84.6 ± 6.5	88.0 ± 6.2	88.8 ± 7.1[a]
Poly(propylene glycol)	0.38	87.7 ± 6.5	89.4 ± 6.7	92.5 ± 6.2	94.1 ± 6.7[a]
Poly(ethylene glycol) diacrylate	0.5	88.5 ± 7.0	90.4 ± 7.2	95.0 ± 6.2	94.7 ± 6.2
Poly(ethylene glycol) 900	0.53	89.2 ± 9.2	88.7 ± 6.2	91.8 ± 6.3	92.9 ± 6.4[a]
α,4-dihydroxy-3-methoxybenzeneacetic acid	0.56	76.0 ± 6.3	67.3 ± 8.7	72.3 ± 6.4	72.6 ± 6.3[a]
Diethylmalonic acid	0.57	89.8 ± 5.6	87.0 ± 6.7	88.6 ± 6.3	89.2 ± 4.2[a]
3,3-dimethylglutaric acid	0.57	98.2 ± 4.3	88.5 ± 6.3	88.5 ± 6.3	89.1 ± 6.9[a]
2,5-hydroxybenzoic acid	0.57	Not observed	Not observed	Not observed	Not observed[a]
Poly(ethylene glycol) 300	0.58	85.6 ± 9.7	83.6 ± 6.5	85.6 ± 6.4	87.6 ± 6.4[a]
Poly(ethylene glycol) 200	0.63	71.3 ± 6.2	77.2 ± 6.3	79.7 ± 6.2	79.8 ± 7.4[a]
Poly(ethylene glycol) bis(carboxymethyl) ether 600	0.63	87.8 ± 7.1	90.4 ± 6.2	90.4 ± 6.6	92.0 ± 6.3[a]
2-methylglutaric acid	0.67	76.7 ± 6.6	76.2 ± 6.3	76.6 ± 6.2	75.3 ± 6.4[a]
2,2-dimethylsuccinic acid	0.67	Not observed	Not observed	Not observed	Not observed[a]
Diethyl-L-tartrate	0.75	86.9 ± 7.3	85.0 ± 6.5	87.4 ± 4.1	90.2 ± 6.6[a]
Glutaric acid	0.8	Not observed	Not observed	Not observed	Not observed[a]
Levoglucosan	0.83	Not observed	Not observed	Not observed	Not observed[a]
Raffinose	0.89	Not observed	Not observed	Not observed	Not observed
Glycerol	1	Not observed	Not observed	Not observed	Not observed[a]
Citric acid	1.17	Not observed	Not observed	Not observed	Not observed[a]
Malonic acid	1.33	Not observed	Not observed	Not observed	Not observed[a]

[a] Data taken from You et al. (2013). All other data are from this study

Figures

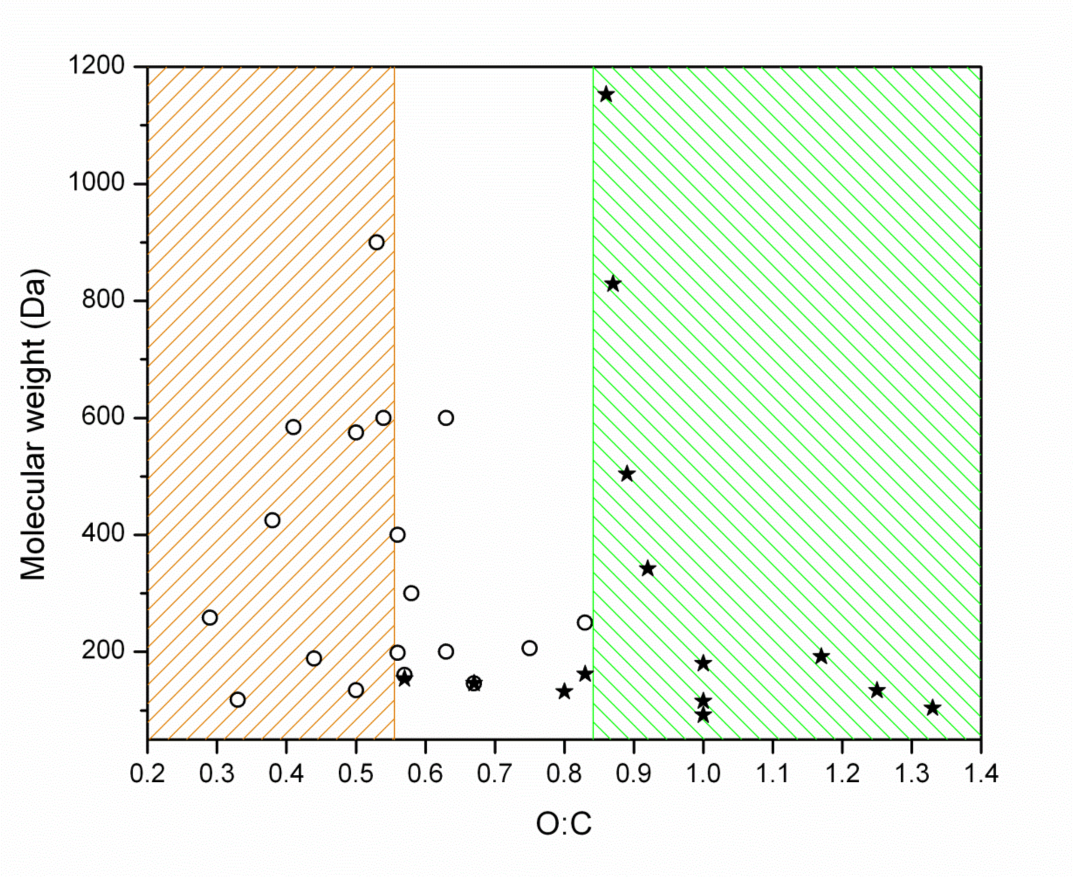

Figure 1 The effect of molecular weight and O:C of the organic species on the occurrence of liquid-liquid phase separation in mixed organic-ammonium sulfate particles (OIR = 2.0 ± 0.1). Data plotted are from the current study and You et al. (2013), and are summarized in Table 3. Open circles indicate liquid-liquid phase separation was observed, while stars indicate liquid-liquid phase separation was not observed. The orange hatched region corresponds to the molecular weight and O:C of the organic species when liquid-liquid phase separation was always observed, and the green hatched region corresponds to the molecular weight and O:C of the organic species when liquid-liquid phase separation was never observed.

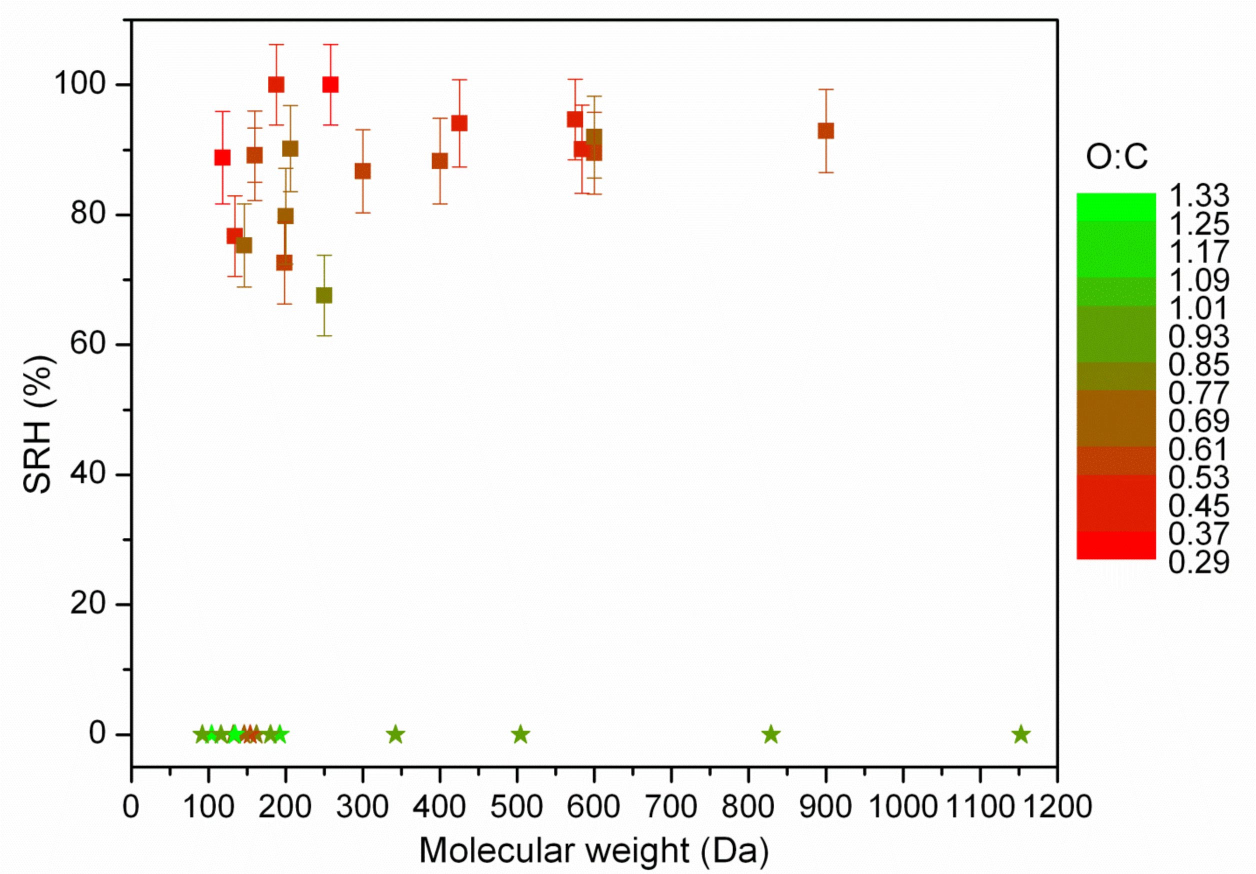

Figure 2. SRH as a function of molecular weight of organic species in the particles at 290 ± 1 K. The SRH results are from the current study and You et al. (2013) (see Table 3). The colors represent the O:C of different organic species. Squares represent SRH of particles in which liquid-liquid phase separation was observed. Bars for the squares are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration. Stars indicate that liquid-liquid phase separation was not observed. OIR = 2.0 ± 0.1in all the experiments.

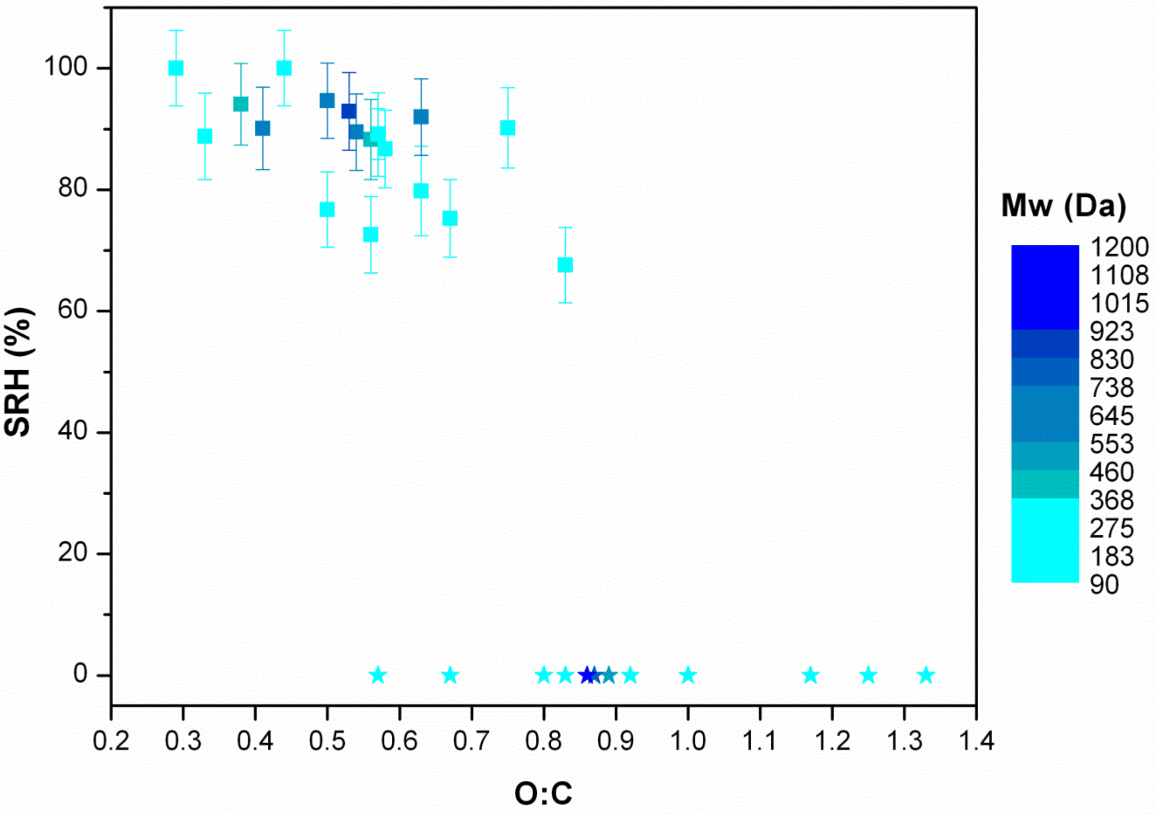

Figure 3. SRH as a function of O:C of the organic species at 290 ± 1 K. The SRH results are from the current study and You et al. (2013) (see Table 3). The colors represent the molecular weight of the different organic species. Squares represent the SRH of particles in which liquid-liquid phase separation was observed. Bars for the squares are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration. Stars indicate liquid-liquid phase separation was not observed. OIR = 2.0 ± 0.1in all the experiments.

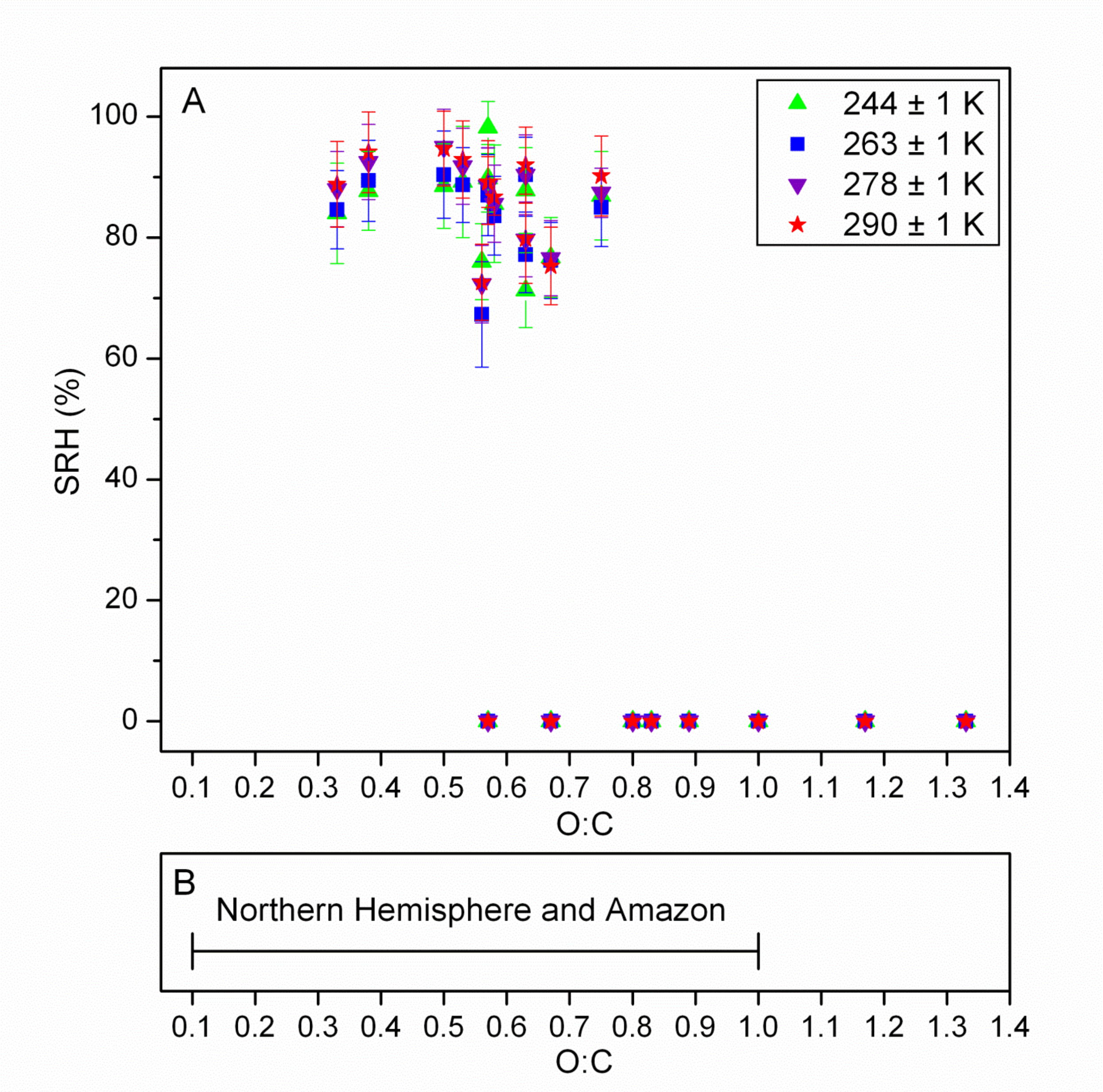

Figure 4. A SRH of mixed organic-ammonium sulfate particles as a function of O:C measured at four different temperatures. Different symbols represent the different temperatures. Bars for the data are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration. Data at SRH= 0% indicate liquid-liquid phase separation was not observed. Data plotted are summarized in Table 4. The OIR = 2.0 ± 0.1 in all the experiments. B Range of the average O:C of organic material in particles from measurements at many locations in the Northern Hemisphere and the Amazon.

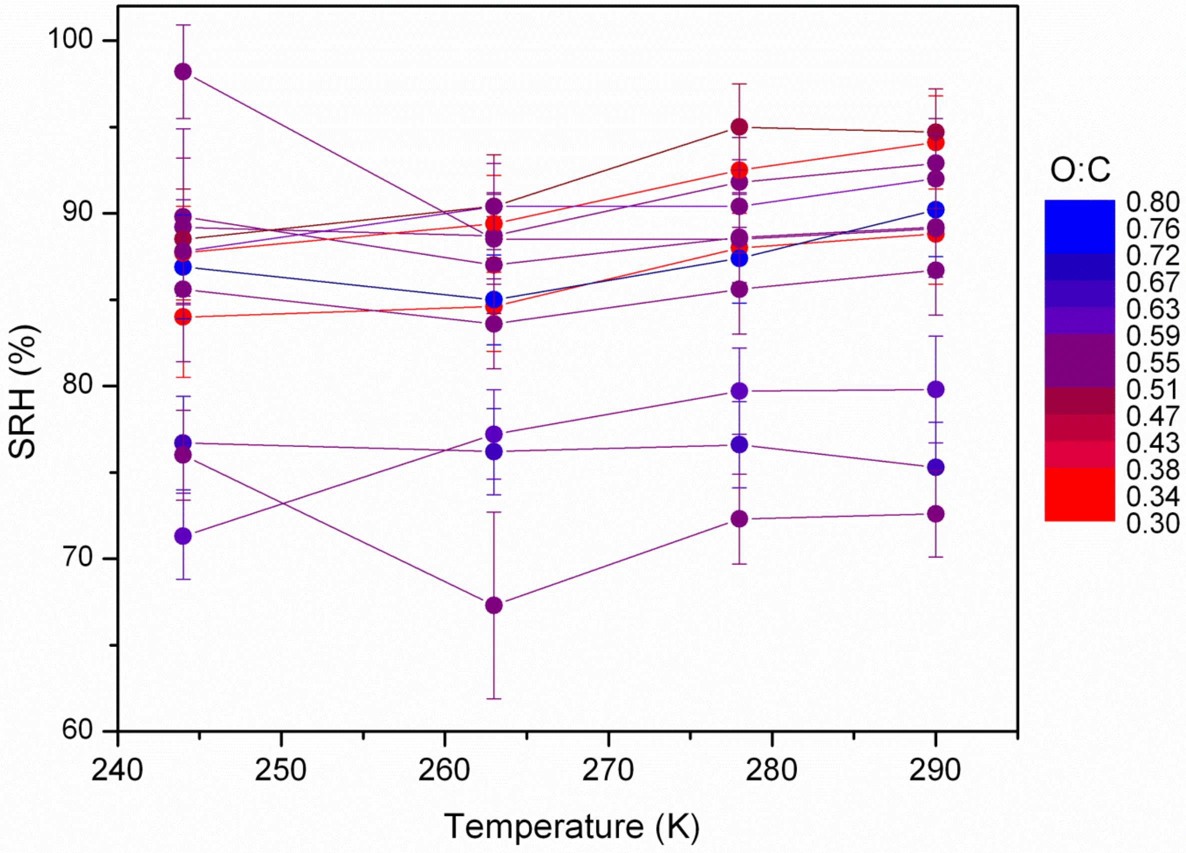

Figure 5. Summary of SRH as a function of temperature for twelve types of mixed organic-ammonium sulfate particles which underwent liquid-liquid phase separation. Data plotted were taken from Table 4. Bars for the data are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration. Colors represent the O:C values of different organic species in the particles. OIR = 2.0 ± 0.1 in all the experiments.

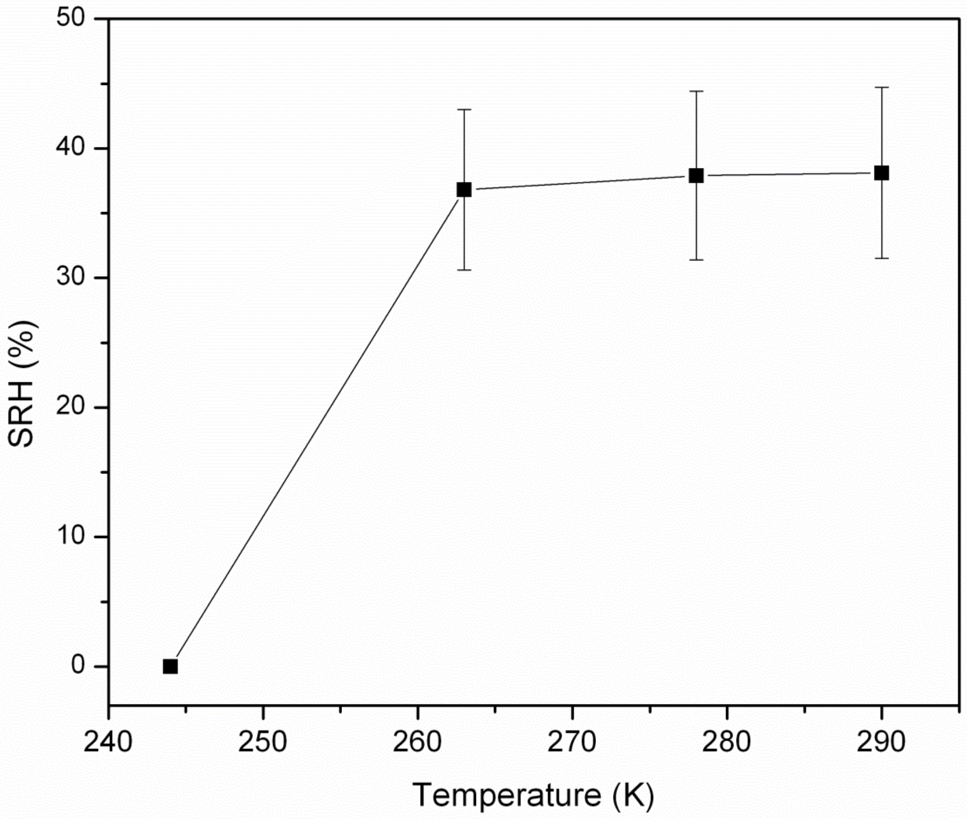

Figure 6 SRH as a function of temperature for particles containing α,4-dihydroxy-3-methoxybenzeneacetic acid mixed with ammonium bisulfate. Bars for the data are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration. Data at 290 ± 1 K was taken from You et al. 2013.

Supplementary Material

Effects of molecular weight and temperature on liquid-liquid phase separation in particles containing organic species and inorganic salts

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1. Linear regression analysis to determine the level of significance of the temperature dependent trends.

To further investigate the effect of temperature on SRH we carried out a linear regression analysis to determine the level of significance of the temperature dependent trends. Shown in Figure S1-S3, are plots of the SRH-values versus temperature for the individual organic compounds studied. Also included in the figure is a linear fit to the data. Listed in Table S1 are the slopes, uncertainties of the slope, correlation coefficients (r) and p-values associated with the fits. In short, 5 out of the 12 systems studied had a high correlation coefficient ($r>0.9$) and low p-value (<0.06).

Supporting tables

Table S1 Summary of the results from the linear regression analysis to understand the relationship between temperature and SRH.

Compounds	Formula	Molecular weight	O:C	Slope	Uncertainty of slope	Correlation coefficient, r	p-value
2,5-hexanediol	$C_6H_{14}O_2$	118.2	0.33	0.12	0.22	0.94	0.06
Poly(propylene glycol)	$C_{3n}H_{6n+2}O_{n+1}$	425	0.38	0.14	0.19	0.99	0.01
Poly(ethylene glycol) diacrylate	$C_{2n+6}H_{4n+6}O_{n+3}$	575	0.5	0.15	0.19	0.94	0.06
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	900	0.53	0.10	0.22	0.88	0.12
α,4-dihydroxy-3-methoxybenzeneacetic acid	$C_9H_{10}O_5$	198.2	0.56	-0.06	0.18	-0.41	0.59
Diethylmalonic acid	$C_7H_{12}O_4$	160.2	0.57	0.00	0.15	-0.07	0.93
3,3-dimethylglutaric acid	$C_7H_{12}O_4$	160.2	0.57	-0.23	0.16	-0.87	0.13
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	300	0.58	0.05	0.23	0.62	0.38
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	200	0.63	0.20	0.19	0.95	0.05
Poly(ethylene glycol) bis(carboxymethyl) ether	$C_{2n+2}H_{4n+2}O_{n+5}$	600	0.63	0.08	0.20	0.94	0.06
2-methylglutaric acid	$C_6H_{10}O_4$	146.1	0.67	-0.02	0.19	-0.72	0.28
Diethyl-L-tartrate	$C_8H_{14}O_6$	206.2	0.75	0.07	0.20	0.67	0.33

Supporting Figures

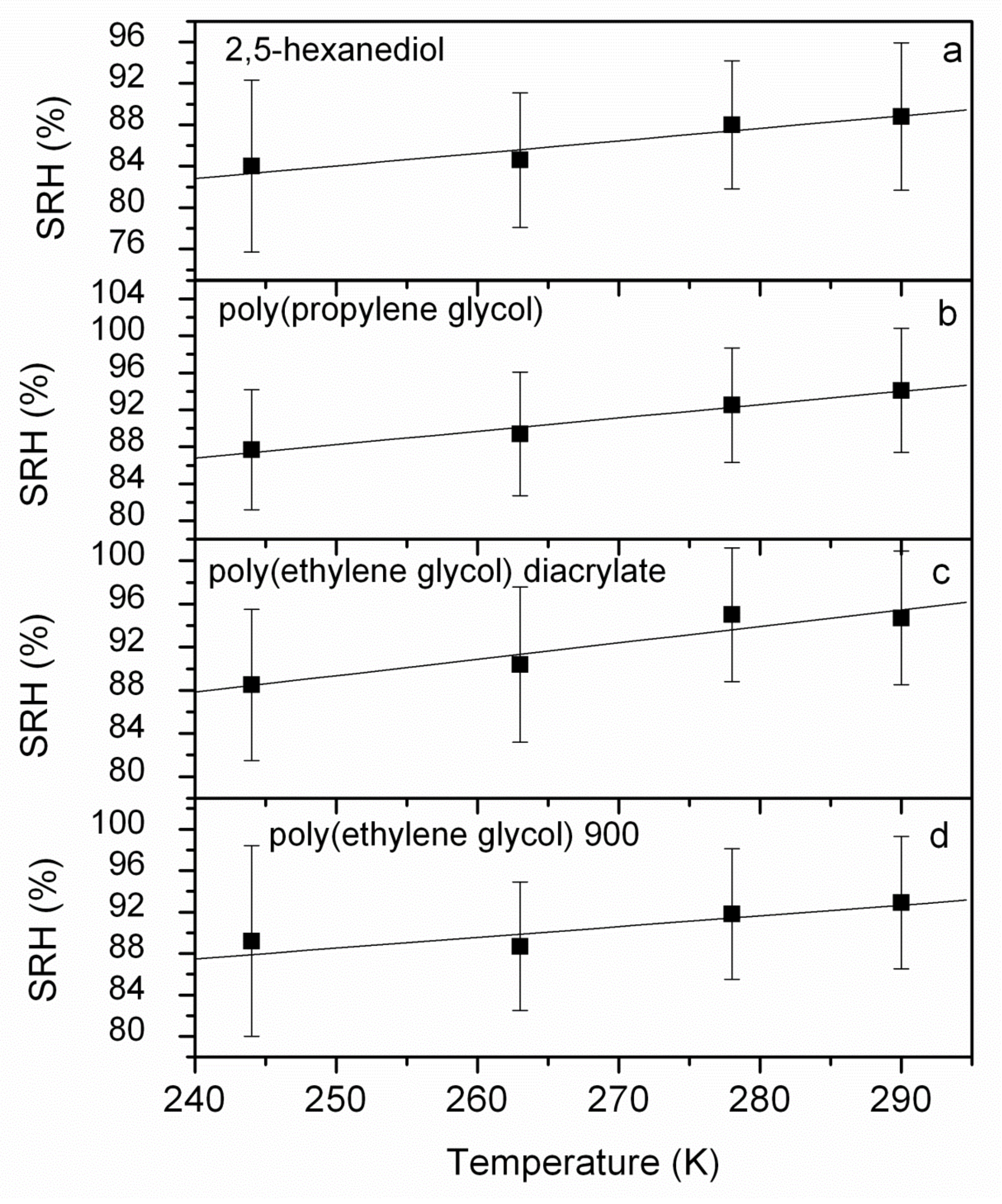

Figure S1 SRH as a function of temperature for particles which underwent liquid-liquid phase separation containing ammonium sulfate mixed with: a) 2,5-hexanediol; b) poly(propylene glycol); c) poly(ethylene glycol) diacrylate; d) poly(ethylene glycol) Mw= 900 Da. Organic species were labeled in each panel. Data plotted were taken from Table 4 of the main text. Bars for the data are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration. OIR = 2.0 ± 0.1 in all the experiments. Black lines are linear fits of SRH as a function of temperature. The results of these linear fits are also shown in Table S1.

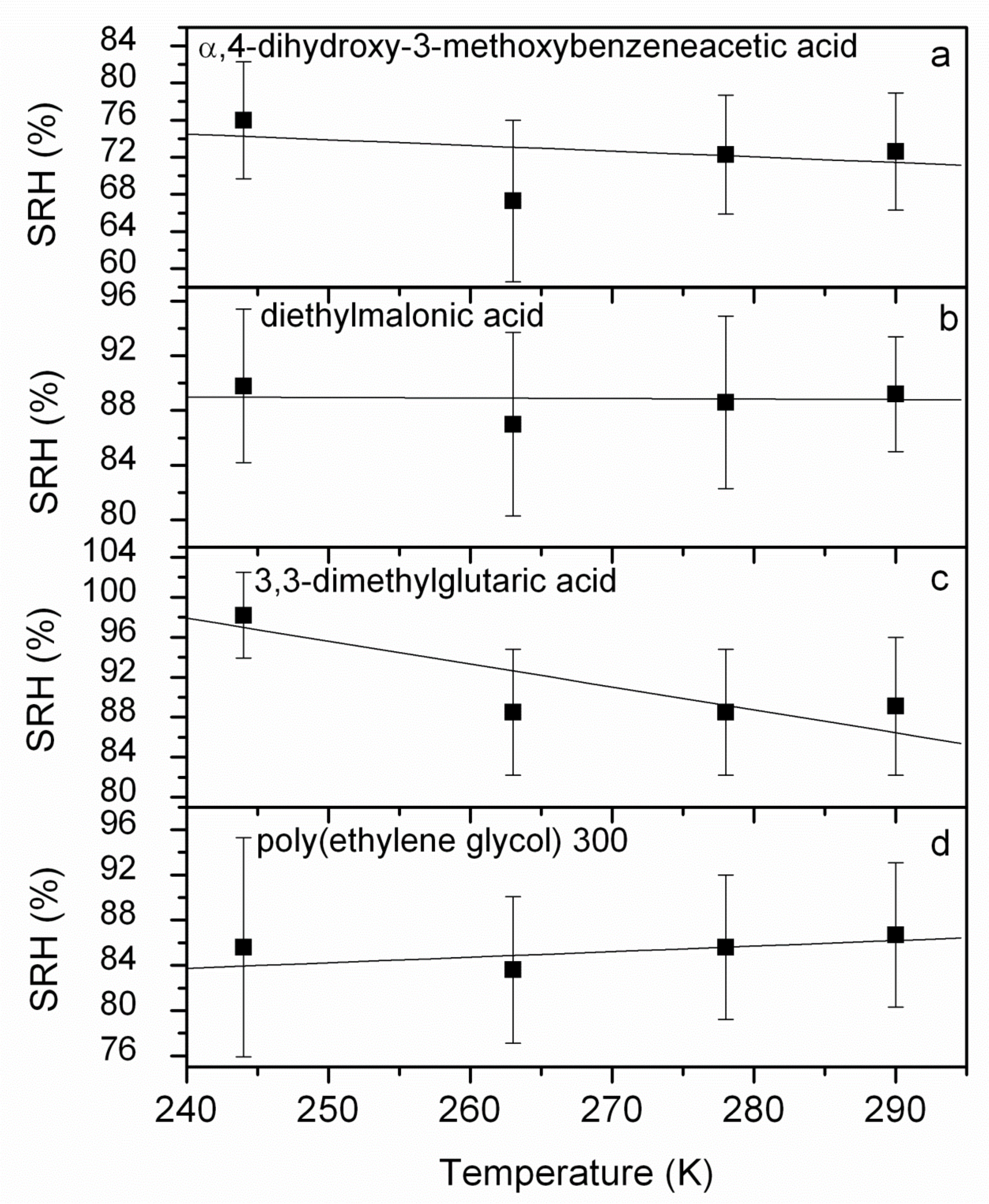

Figure S2 SRH as a function of temperature for particles which underwent liquid-liquid phase separation containing ammonium sulfate mixed with: a) α,4-dihydroxy-3methoxybeneacetic acid; b) diethylmalonic acid; c) 3,3-dimethylglutaric acid; d) ploy(ethylene glycol) Mw= 300 Da. Organic species were labeled in each panel. Data plotted were taken from Table 4 in the main text. Bars for the data are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration. OIR = 2.0 ± 0.1 in all the experiments. Black lines are linear fits of SRH as a function of temperature. The results of these linear fits are also shown in Table S1.

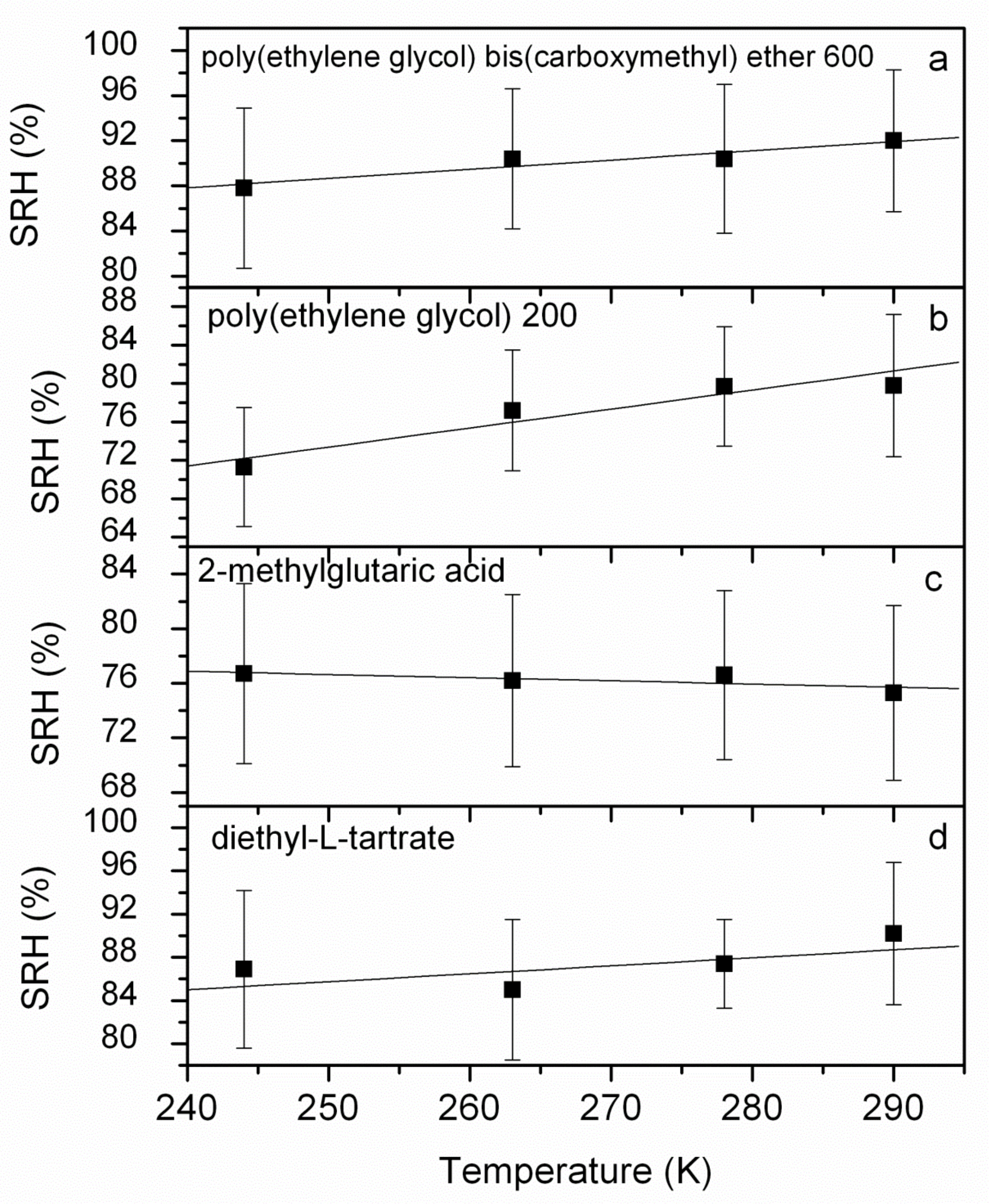

Figure S3 SRH as a function of temperature for particles which underwent liquid-liquid phase separation containing ammonium sulfate mixed with: a) poly(ethylene glycol) bis(carboxymethyl) ether Mw=600 Da; b) poly(ethylene glycol) Mw= 200 Da; c) 2-methylglutaric acid; d) diethyl-L-tartrate. Organic species were labeled in each panel. Data plotted were taken from Table 4 in the main text. Bars for the data are 95% confidence intervals considering σ of multiple SRH measurements and the uncertainty from the calibration. OIR = 2.0 ± 0.1 in all the experiments. Black lines are linear fits of SRH as a function of temperature. The results of these linear fits are also shown in Table S1.